

UDC 666.293.522.5

## JEWELRY ENAMELS WITH A DECREASED CONTENT OF LEAD OXIDE

S. P. Rodtsevich,<sup>1</sup> S. Yu. Eliseev,<sup>1</sup> and G. F. Lukashevich<sup>1</sup>Translated from *Steklo i Keramika*, No. 8, pp. 27–28, August, 2001.

The effect of aluminum and cadmium oxides on glasses in an alkali-bearing lead-boron-silicate system is considered. The effect of the ratio between aluminum and cadmium oxides on the enamel tint and on some physicochemical and technological parameters is demonstrated. It is established that the specified system can be used to produce a low-melting (780–800°C) sky-blue corrosion-resistant enamel for copper and copper alloys.

Jewelry enamels are widely used in production of decorative articles made of non-ferrous metals. The existing colored enamels for jewelry are rather expensive, have a high content of lead oxide (20–65%) [1–3], and are fused within a wide temperature range (700–950°C). Their synthesis is based on the lead-silicate system, in which  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , and  $\text{SnO}_2$  are used as opacifiers [3, 4].

Of special interest are jewelry enamels using fluorine as an opacifier (it is more available than other opacifiers) and containing smaller quantities of lead and boron oxides.

The purpose of the present paper was to develop a jewelry enamel in the system  $\text{SiO}_2 - \text{B}_2\text{O}_3 - \text{R}_2\text{O}_3 - \text{RO} - \text{R}_2\text{O} - \text{F}^-$ . The amount of basic oxides in the considered compositions was as follows (here and elsewhere mass content): 35.0–52.0  $\text{SiO}_2$ , 5.0–7.0  $\text{B}_2\text{O}_3$ , 0.18–3.2  $\text{Sb}_2\text{O}_3$ , 4.0–4.5  $\text{PbO}$ , 3.5–7.5  $\text{CdO}$ , 15.0–20.0  $\text{R}_2\text{O}$  ( $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ), 9.0–15.0 F. The sum of the pigment oxides ( $\text{Cr}_2\text{O}_3 + \text{Co}_2\text{O}_3 + \text{CuO}$ ) did not exceed 2.5%. With the aim of modifying the compositions (to obtain a prescribed color tint), up to 6% aluminum oxide was introduced in some compositions at the expense of silicon oxide.

The glasses were synthesized in an electric furnace with silite heaters at a temperature of 1250–1350°C with an exposure at the maximum temperature for 35 min. The glasses were melted in porcelain crucibles of 250-ml capacity. After

the filament quality test, the glass was molded in the form of tiles on a steel slab. The tiles were then milled, and the glass powder was deposited on a tombac alloy substrate according to the standard technology for jewelry enamels [1, 2]. The firing temperature was 780–820°C, and the firing duration was 3–5 min.

The resulting glass was opacified. The x-ray phase analysis determined that NaF is the main crystalline phase and  $\text{K}_2\text{NaAlF}_6$  is present in small quantities. An increase in the fluorine content has a favorable effect on the properties of enamel, facilitating homogeneous spreading and the smoothness of the coating.

It is established that by varying the ratio of fluorine to alkaline oxides and aluminum and cadmium oxides while the content of pigment oxides remains constant, it is possible to produce jewelry enamels of various tints from sky-blue to turquoise and to greenish-blue. The reflection coefficient of the synthesized coatings is 70–75%. A sky-blue coating with a high degree of luster (70%) was obtained when the ratio  $\text{Al}_2\text{O}_3 : \text{CdO}$  was equal to 2 : 1 (the pigment oxide sum 2.3%) and the glass contained 4.3%  $\text{PbO}$ , 6.5%  $\text{B}_2\text{O}_3$ , and 13.5% F.

Increasing the fluorine content up to 15% by decreasing the alkaline oxides sum to 17% causes a modification in the coating tint from sky-blue to greenish-blue. An increase in the content of cadmium or aluminum oxides at the expense of silicon oxide with a constant content of boron and lead oxides leads to an increased TCLE but lowers the chemical

<sup>1</sup> Institute of General and Inorganic Chemistry, National Academy of Sciences of Belarus, Minsk, Belarus.

TABLE 1

Compositions	Weight content, %				Chemical resistance (grain weight loss), %	TCLE, $10^{-7} \text{ K}^{-1}$	Softening start temperature, °C
	$\text{Al}_2\text{O}_3$	$\text{CdO}$	$\text{SiO}_2$	$\text{Na}_2\text{O} + \text{K}_2\text{O}$			
100	6.05	3.54	42.48	18.89	0.79	120.0	520
105	—	7.59	48.13	17.04	0.35	113.9	500
108	2.58	3.53	46.94	19.11	0.32	111.2	530
110	1.73	3.53	48.01	18.69	0.30	110.6	520
111	—	—	52.08	18.44	0.32	114.1	530

resistance of glass (the chemical resistance of glasses was determined by the grain method with respect to 4% acetic acid according to GOST 10134.0.82 – GOST 10134.2.82). The initial temperature of glass softening and the reflection coefficient of the coating varies insignificantly. The coating reflection coefficient of composition 100 is 70%, and that of compositions 105 – 111 is 75%. The spreadability of enamels is within the limits of 45 – 63 mm (spreadability was determined according to GOST 24405–80).

Let us consider a number of studied samples as examples (Table 1). It can be seen that there is no unique dependence of the properties on the composition of the glass. One can only infer the effect of a particular oxide on the properties of glass and coating.

Additional data on the glass structure are provided by IR spectroscopy (Fig. 1). The IR spectra of glasses exhibit intense absorption bands with maximums at 1080–1040, 485–475, and 625–610  $\text{cm}^{-1}$  and less intense maximums in the ranges 1450–1300 and 800–700  $\text{cm}^{-1}$ .

The wide absorption band in the ranges 1080–1040 and 485–475  $\text{cm}^{-1}$  corresponds to the oxygen-silicon tetrahedrons  $\text{SiO}_{4/2}$  [5]. The presence of absorption bands in the range 1450–1300  $\text{cm}^{-1}$  with a maximum at 1350–1400  $\text{cm}^{-1}$  correlates with the vibrations of three-coordination boron atoms in  $\text{BO}_{3/2}$  groups [6]. The absorption bands in the range 600–625  $\text{cm}^{-1}$  are attributed to the vibrations in four-coordination boron groups  $\text{BO}_{4/2}$  [6–8]. The absorption bands with maximums at 715–705  $\text{cm}^{-1}$  indicate the presence of four-coordination aluminum groups  $\text{AlO}_{4/2}$  [5]. The presence of absorption groups in the range 775–820  $\text{cm}^{-1}$  is difficult to account for uniquely. Some authors attribute them to the bond vibrations in lead silicate  $\text{PbO} \cdot \text{SiO}_2$  [9]. In studying the IR absorption spectra of pure NaF, no characteristic absorption bands were registered.

The IR spectra shown in Fig. 1 can be interpreted as follows. The spectrum of composition 100 points to the presence of silicon-oxygen groups  $\text{SiO}_{4/2}$ , a certain quantity of three-coordination boron  $\text{BO}_{3/2}$ , a much larger quantity of four-coordination boron  $\text{BO}_{4/2}$  and four-coordination aluminum  $\text{AlO}_{4/2}$  incorporated in the common silicon-aluminum-boron-oxygen lattice. Apparently, one can speak of a certain quantity of lead silicates. But considering the ratio of absorption-band intensities of  $\text{SiO}_{4/2}$  and  $\text{PbO} \cdot \text{SiO}_2$ , the amount of the latter is insignificant and clearly insufficient for its identification in the x-ray phase analysis.

Compositions 105 and 111 do not contain aluminum; accordingly, they have no absorption bands in the range 715–705  $\text{cm}^{-1}$ .

The aluminum oxide content in compositions 108 and 110 consecutively decreases and, accordingly, the quantity of three-coordination boron decreases as well (the absorption bands at 1400–1350  $\text{cm}^{-1}$  disappear). Apparently, the competition for alkaline oxides becomes weaker and, accordingly, the probability of boron existing in the four-coordination state becomes higher. The absorption bands in the range 600–625  $\text{cm}^{-1}$ , which are associated with atom vibrations

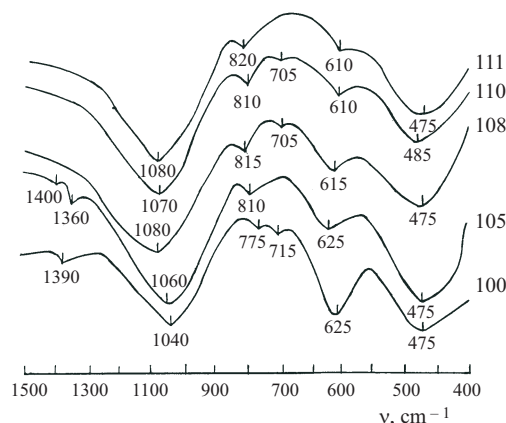


Fig. 1. IR spectra of glasses in  $\text{SiO}_2 - \text{B}_2\text{O}_3 - \text{R}_2\text{O}_3 - \text{RO} - \text{R}_2\text{O} - \text{F}^-$  system.

in  $\text{BO}_{4/2}$  groups, persist, although their intensity does not increase (the boron oxide content is virtually equal in all compositions). The same is true of this absorption band in composition 111, i.e., the presence of aluminum oxide in glass makes the glass lattice structure more complex due to the incorporation of aluminum in the glass lattice and also owing to the fact that not all boron in the presence of aluminum is converted to four-coordination form. The glass lattice in this case becomes looser and, accordingly, less chemically resistant.

As a result of the studies performed, sky-blue and turquoise corrosion-resistant jewelry enamel compositions were developed for copper and copper alloys. Composition 100, which is the most suitable for specific production needs, has been used in manufacturing the Matsi State Order of the Republic of Belarus.

## REFERENCES

1. *Enameling of Metal Articles* [in Russian], Mashinostroenie, Leningrad (1972).
2. É. Brepol', *Artistic Enameling* [Russian translation], Mashinostroenie, Leningrad (1986).
3. A. Petzold and G. Peschmann, *Enamel and Enameling* [Russian translation], Metallurgiya, Moscow (1990).
4. E. Ya. Yatsenko, A. M. Kondyurin, V. P. Rat'kova, and N. M. Tkachenko, "Decorative enamels for copper," *Steklo Keram.*, No. 3, 25 – 27 (1997).
5. V. A. Kolesova, "Infrared absorption spectra of silicates containing aluminum and certain crystalline aluminosilicates," *Opt. Spektrosk.*, 6, Issue 1, 38 – 44 (1959).
6. I. I. Plyusnina and Yu. A. Kharitonov, "Crystalline specifics and infrared absorption spectra of borate and borosilicate," *Zh. Strukt. Khim.*, 4(4), 555 – 568 (1963).
7. A. A. Appen, *Chemistry of Glass* [in Russian], Khimiya, Leningrad (1974).
8. T. S. Petrovskaya, P. S. Kalinin, R. S. Shchelevich, and V. I. Vereshchagin, "A study of the structure of lead-boron-silicate glasses by the NMR and infrared spectroscopy methods," *Fiz. Khim. Stekla*, 10(2), 150 – 154 (1984).
9. *Infrared Spectra of Inorganic Glasses and Crystals* [in Russian], Khimiya, Leningrad (1972).